UNIVERSITY OF PENNSYLVANIA

THE EFFECT OF IRON AND OXYGEN ON THE ELECTRICAL CONDUCTIVITY OF COPPER

RUSSELL P. HEUER

A THESIS

PRESENTED TO THE FACULTY OF THE GRADUATE SCHOOL IN
PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

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INTRODUCTION

The electrical conductivity of dilute solid solutions of metallic elements in copper has been the subject of many investigations. The data presented treat the binary systems of copper and practically every metal which may occur as impurity in commercial copper: viz., Silver, Gold, Zinc, Cadmium, Aluminum, Tin, Phosphorus, Arsenic, Antimony, Iron, Cobalt and Nickel. (Guertler, *Handbuch der Metallographie*, Berlin; Circular No. 73, Copper, U. S. Bureau of Standards.)

Unfortunately the alloys measured have been contaminated with cuprous oxide as a soluble component in the liquid phase, the oxide being formed during melting by action of the furnace gases and during casting by action of the atmosphere. This oxide tends to establish equilibrium with the solute metal, whereby some of the solute is oxidized and may exist in the solidified alloy as non-metallic inclusion. The amount of such inclusion has been generally neglected in the reported conductivity measurements. A preliminary thermodynamic calculation will serve to show that for many elements this oxide cannot be neglected. As an illustration, the calculation will be made for the solute element iron.

In accordance with the general relationship, the copper oxide dissolved in the melt is dissociated thus

$$Cu_2O\ (c_1) \rightarrow 2\ Cu\ (c_2) + \tfrac{1}{2}\ O_2 \quad \ldots\ldots (1)$$

The oxygen partial pressure at equilibrium is determined by the equation

$$\Delta F_T^\circ = -\ RT \ln \frac{a^2\ Cu \cdot a^{\frac{1}{2}}\ O_2}{a\ Cu_2O} \quad \ldots\ldots (2)$$

The solute is subjected to this oxygen partial pressure according to the reaction

$$Fe\ (c_3) + \tfrac{1}{2}\ O_2 \rightarrow FeO \quad \ldots\ldots (3)$$

To attain equilibrium, the liquid metal phase may loose iron and oxygen, the ferrous oxide being insoluble. The condensed reaction may be written

$$Cu_2O\ (c_1) + Fe\ (c_3) \rightarrow FeO + 2\ Cu\ (c_2) \quad \ldots\ldots (4)$$

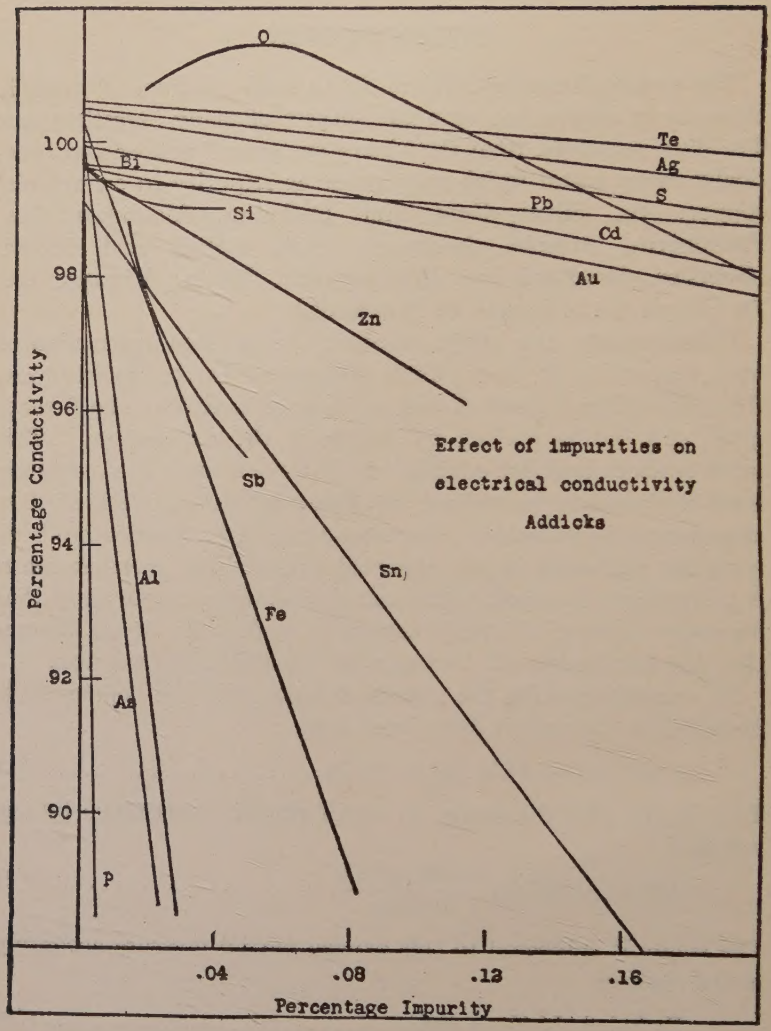
O
Te
Ag
S
Pb
Cd
Au
Bi
Si
Zn
Sb
Sn
Fe
Al
As
P
100
98
96
94
92
90
Percentage Conductivity
Effect of impurities on
electrical conductivity
Addicks
.04
.08
.12
.16
Percentage Impurity

FIG. 1

Equilibrium is expressed as in (2)

$$\Delta F_T^\circ = -RT \ln \frac{a^2 Cu \cdot a FeO}{a Cu_2O \cdot a Fe} \quad \ldots\ldots\ldots\ldots\ldots\ldots (5)$$

Eastman (*J. A. C. S.*, 44 (1922), 875) examined critically the recorded data for equilibria in the reaction

$$FeO\ (S) + CO \rightarrow Fe\ (S) + CO_2. \quad \ldots\ldots\ldots\ldots\ldots\ldots (6)$$

From Lewis value of $\triangle F^\circ$ for the reaction

$$CO + \tfrac{1}{2} O_2 \rightarrow CO_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots (7)$$

(Lewis & Randall, *Thermodynamics*, New York, 1923) he concludes for the reaction

$$FeO\ (S) \rightarrow Fe\ (S) + \tfrac{1}{2} O_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots (8)$$

$$\Delta F^\circ_{378} = 49{,}700 \text{ calories}$$
$$\Delta F^\circ_{973} = 48{,}075 \quad \text{“}$$
$$\Delta F^\circ_{1073} = 46{,}445 \quad \text{“}$$
$$\Delta F^\circ_{1173} = 44{,}840 \quad \text{“}$$
$$\Delta F^\circ_{1273} = 43{,}255 \quad \text{“}$$

Roberts and Smyth (*J. A. C. S.*, 43 (1921), 1061) investigated the equilibria of the system copper, oxygen. For the reaction

$$Cu_2O\ (S) \rightarrow 2\ Cu\ (c_2) + \tfrac{1}{2} O_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots (9)$$

they record the oxygen pressures

1392.3° K	0.028 mm. Hg
1423.5° K	.035 “ “
1457.1° K	.041 “ “

From these data, ΔF° of equation (9) and finally for equation (5) may be calculated. For the present purpose Cu_2O (S), Cu (L), Fe (S), FeO (S) are chosen as the standard states of unit activity. The temperatures calculated are 1063° C. and 1125° C., being respectively the temperatures assumed for the eutectic and for the formation of the liquid alloy. The calculation yields

$$\Delta F^\circ_{1336} = -24{,}800 \text{ calories} \quad \ldots\ldots\ldots\ldots\ldots\ldots (10)$$
$$\Delta F^\circ_{1398} = -23{,}800 \quad \text{“} \quad \ldots\ldots\ldots\ldots\ldots\ldots (11)$$

From equation (5), the equilibrium values are

$$a\,Fe\ (1336°) = 8 \times 10^{-5} \quad (12)$$
$$a\,Fe \times a\,Cu_2O\ (1398°) = 19 \times 10^{-5} \quad (13)$$

In the absence of data relating the activity of iron and cuprous oxide in copper solutions to the mol fraction, these equilibrium concentrations cannot be calculated.

Sahmen (*Zts. fur anorg. chem.*, 57 (1908), 1) reports in the phase diagram of the copper-iron system the limit of solubility of iron in copper-rich liquid and likewise in solid solution as approximately three per cent. With this condition, the activity of iron doubtless exceeds its mol fraction. Hence, by equation (12) the equilibrium concentration for iron in the presence of cuprous oxide at the eutectic temperature must be less than 0.008% by weight. Liquid alloys may contain iron in excess of this value at higher temperatures such as 1125° C., provided the requirements of equation (13) are satisfied. Upon cooling these alloys to the eutectic temperature, the excess of iron must react to form iron-oxide. Either the cuprous oxide will disappear or the excess iron be used up, provided sufficient time elapses at the eutectic temperature for the reaction to be completed.

With this preliminary picture, the data for the conductivity of copper-iron alloys as recorded by Addicks (*Tr. A. I. M. E.*, 36 (1906), 18) may be reviewed.

Iron, per cent	Copper, per cent	Conductivity (referred to Standard), per cent
0.0	99.89	100.5
0.042	99.93	96.8
0.046	99.90	92.9
0.068	99.89	89.6

These alloys were melted in a fuel-fired furnace and cast in the atmosphere. They certainly contained oxygen. From the measurements, Addicks calculates a numerical factor, designed to express the ratio of per cent lowering of electrical conductivity to per cent of iron present. Despite appreciable discordance among the alloys measured, he evaluates the factor at 140. Naturally some of the iron present in his alloys has been converted to oxide.

This oxide causes the discordant results and in addition yields too low a value for the factor.

Addicks' methods for iron solid solutions, and no doubt for

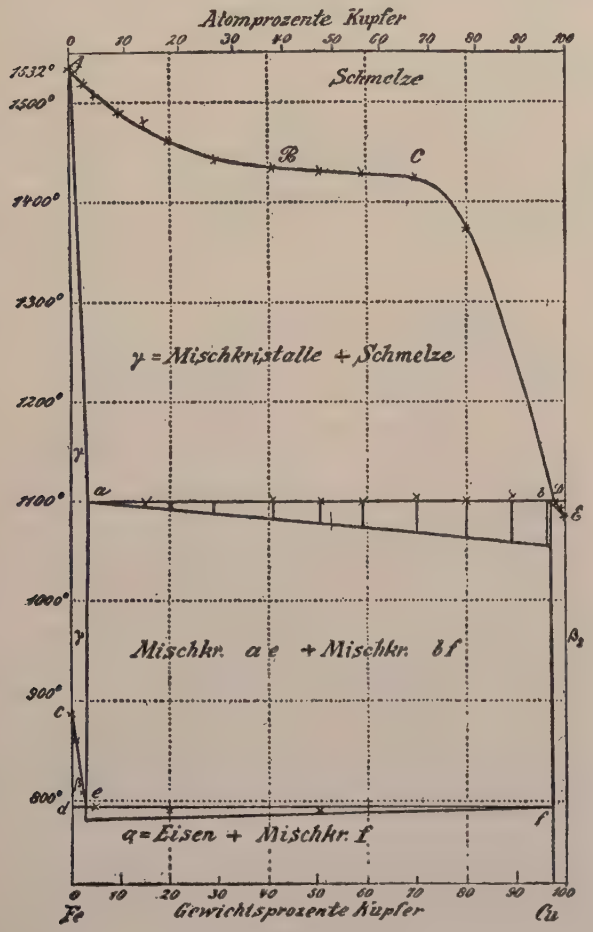

FIG. 2

many of the other elements reported in his original paper, are inadequate. The effect of oxygen cannot be neglected. It would be better to include the oxygen as part of the system, and base

the iron alloys upon the ternary system copper, iron, oxygen. The specific effect of both iron and oxygen would then be evaluated.

In the present work, it is planned to apply this method. The copper-rich alloys of the binary systems copper-iron and copper-cuprous oxide, are first measured for conductivity. Then the ternary alloys are investigated. Equations (12) and (13) are used to interpret the data.

Experimental

Pure copper for the alloys was prepared by two successive electrolytic depositions of the metal. Pure electrolyte free of metallic impurities was used in the final deposition—The Cathodes analyzed:

Ag — 0.0003%	Ni — 0.0001%
As — 0.0000	Zn — 0.0000
Sb — 0.0001	Pb — 0.0000
Bi — 0.0000	S — 0.0004
Fe — 0.0001	Se + Te — 0.0000
Co — 0.0000	

The melts were prepared in a platinum resistance furnace having a vertical heating chamber 12 inches high, 3 inches diameter. The furnace was evacuated and filled with dry, oxygen-free nitrogen. The system of crucibles and feeders used is shown in Fig. 3. For the binary series copper-iron, electrolytic iron chips to form the desired alloy were placed in the thimble (*b*). The feeder (*a*) contained 375 grams of copper and 300 grams of anhydrous barium chloride. Seven hours were required for making each melt, 3¼ hours for heating to 1125° C., ¾ hour at that temperature and four hours for slow cooling. Practically all the cuprous oxide was removed from the liquid metal by the solvent action of the molten barium chloride.

The solidified melts were sampled for metallographic specimens and forged hot to $\frac{5}{8}$-inch octagon section. Scale and surface defects were removed by machining to $\frac{9}{16}$-inch diameter, whereupon the samples were annealed at 950° C. for fifty hours in carbon dioxide to equalize any cored structure present in the original dendrites. The forgings were then drawn cold to 12 gauge (.080-inch diameter) wire and annealed at 500° C. by passing an

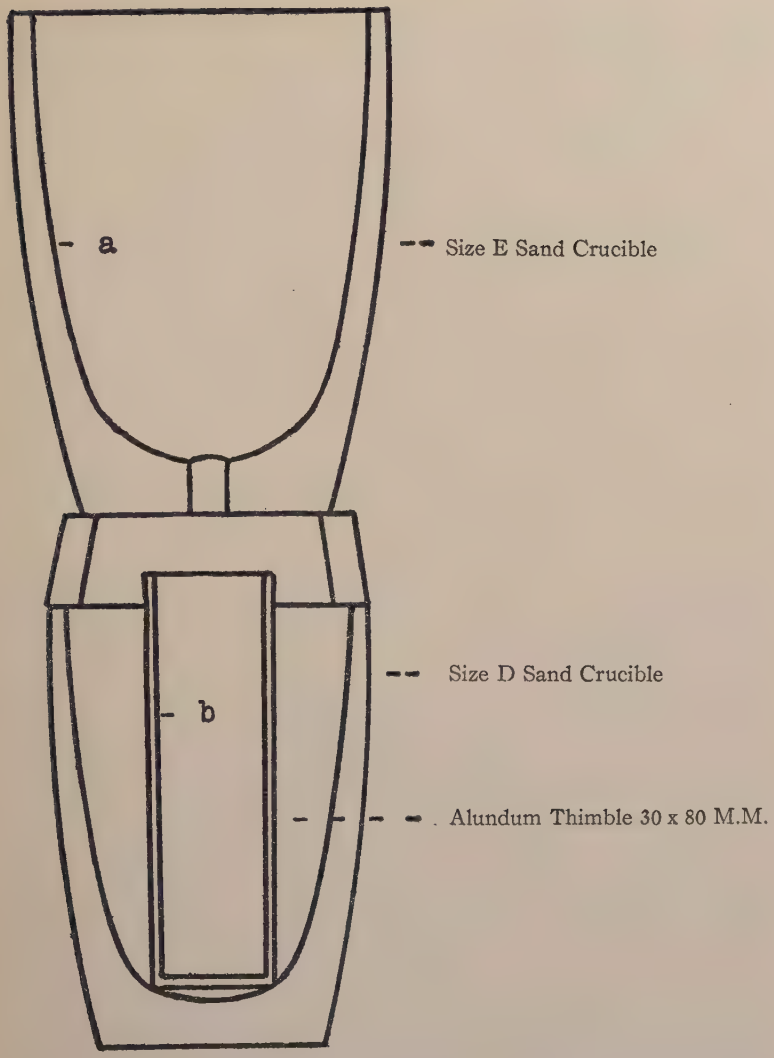

FIG. 3

Crucible Assembly

electric current through the wire. The conductivity was measured at 20° C., using the standard bridge. 0.15328 ohms per meter gram was considered 100% conductivity.

Chemical analyses for copper, oxygen, sulphur and iron were made on each melt. Copper was determined on turnings removed from the cast piece. Two 10-gram electrolytic assays were made, checking within 0.003%. Oxygen and sulphur were determined by ignition in hydrogen at 900° C. to convert these elements to water and hydrogen sulphide. (Bassett and Bedworth, *Tr. A. I. M. E.*, 73 (1926), 784.) The sulphide evolved was absorbed in ammoniacal cadmium chloride solution and evaluated by iodine titration. The loss in weight of the sample upon this ignition was attributed to oxygen and sulphur. Knowing the sulphur value, oxygen was determined by difference.

Sixty grams of wire samples from the conductivity measurements were used in this analysis. After cleaning the metal surface, as recommended, with abrasive, dilute alcoholic potassium hydrate, dilute potassium cyanide, distilled water, alcohol and ether, there was no assurance that upon drying at 80° C. the surface would be free of oxide or adsorbed substances. That adsorbed substances were present, seemed proved when metal so prepared was ignited in carbon dioxide and lost 0.0008% in weight. Since all material volatile in carbon dioxide from within the copper had been removed by previous annealing at 950° C. for fifty hours, this loss must have been a surface effect. Upon further ignition in hydrogen at 900° C. for five hours, this piece lost 0.0006% as oxygen. Some of this might have been surface oxygen. To overcome these surface effects, a similar sample was given a rapid preliminary heating in hydrogen to 550° C., held for three minutes and cooled rapidly. This freed the adsorbed material and removed surface oxygen. Upon further treatment at 900° C. for five hours, 0.0004% oxygen was lost. From this, the preliminary hydrogen heating was considered more satisfactory than ether drying and carbon dioxide ignition, where such small amounts of oxygen were involved. Iron was determined on the conductivity samples, after electrolytically removing the copper, by double precipitation with gaseous ammonia and weighing as ferric oxide.

It was found impossible to use the crucible assembly shown in

Fig. 3 for making copper free of iron due to a considerable "pick-up" of iron from the crucible. To overcome this, a silica tube ten inches long, seven-eights inch inside diameter, sealed at one end was substituted for the crucibles. Two hundred gms. of copper and 75 gms. of barium chloride were charged. The copper used was specially freed of sulphur by ignition in hydrogen. The melt piped badly but sufficient metal for one conductivity measurement was obtained.

For the binary series copper-cuprous oxide, methods similar to those employed for the copper-iron series were used. The charge, of course, contained no iron addition and no barium chloride. The oxygen addition was made by allowing the desired amount of oxygen gas to be present in the nitrogen atmosphere of the furnace. No annealing of the forged pieces for 50 hours at 950° C. was required. In the oxygen determination, ether drying at 80° C. was used for preparation of the sample.

TABLE 1

Melt No.	Copper, weight, per cent	Oxygen, weight, per cent	Sulphur, weight, per cent	Iron, weight, per cent	Iron, atomic, per cent	Conductivity, per cent
22	100.000	0.0002	0.0001	0.0002	0.0002	102.10
4	99.995	0.0007	0.0006	0.0071	0.0080	97.60
3	99.975	0.0007	0.0006	0.0241	0.0274	90.05
20	99.880	0.0002	0.0003	0.1212	0.1379	64.80
18	99.778	0.0001	0.0001	0.2179	0.2481	49.6
21	99.159	0.0003	0.0004	0.814	0.925	35.6

For the ternary alloys, the methods of the copper-cuprous oxide series were adopted. A copper-iron alloy containing 2.2% iron was used for the iron addition. The amount desired was charged in the feeder crucible.

RESULTS

The data for the binary system copper-iron are assembled in Table I. The curve of Fig. 4 expresses the relationship of conductivity to atomic per cent of iron. The form of this curve is in accord with the general behavior of solid solutions as expressed by Guertler (*op. cit.*). For comparison the data of Addicks are also plotted. The curve indicated by his results exhibits approx-

imately the same slope as the curve presented here. Addicks' curve, however, suffers a lateral displacement toward higher iron values. This displacement confirms the original premise of this paper that ferrous oxide was present in these alloys. It further suggests that Addicks' data for the solid solutions of elements other than iron might also be in similar error.

The effect of small additions of iron upon the conductivity is shown to be considerable. No constant factor expressing the ratio of lowering in conductivity to per cent iron is obtainable

TABLE 2

Melt No.	Copper, weight, per cent	Oxygen, weight, per cent	Sulphur, weight, per cent	Iron, weight, per cent	Cuprous Oxide	
					Weight (calculated), per cent	Volume (calculated), per cent
22	100.000	0.0002	0.0001	0.0002	0.0018	0.003
7	99.980	0.0201	0.0002	0.0003	0.180	0.267
6	99.912	0.0889	0.0004	0.0003	0.800	1.181
5	99.876	0.1266	0.0002	0.0002	1.133	1.670
9	99.664	0.3373	0.0002	0.0002	3.019	4.411

Melt No.	Conductivity, per cent	Resistivity, $\frac{\text{ohms}}{\text{meter, gram}}$	Density (calculated)	Conductivity (observed) $\frac{\text{ohms}^{-1}}{\text{cm}^3} \times 10^{-6}$	Conductivity (calculated) $\frac{\text{ohms}^{-1}}{\text{cm}^3} \times 10^{-6}$	Conductivity (obs'v'd minus) (calculated) $\frac{\text{ohms}^{-1}}{\text{cm}^3} \times 10^{-6}$
22	102.1	0.15013	8.89	0.5921	0.5921	0.0000
7	101.8	0.15057	8.881	0.5898	0.5905	−0.0007
6	100.8	0.15207	8.852	0.5821	0.5855	−0.0034
5	100.25	0.15292	8.834	0.5777	0.5822	−0.0045
9	97.9	0.15657	8.757	0.5593	0.5660	−0.0067

due to the changing slope of the curve. For the first 0.0071% iron present, the conductivity is lowered 4.5%—corresponding to a factor of 634. This great depression tends toward agreement with Norbury's (*Tr. Farad. Soc'y*, 16 (1921), 570) generalization that solute elements far removed in the periodic system from the solvent metal cause the greater lowering in conductivity.

Sample 22, the purest copper obtained in these experiments has a conductivity of 102.1%. This can be compared with the values assembled by Wolff and Dellinger (*U. S. Bur. of Stds.*,

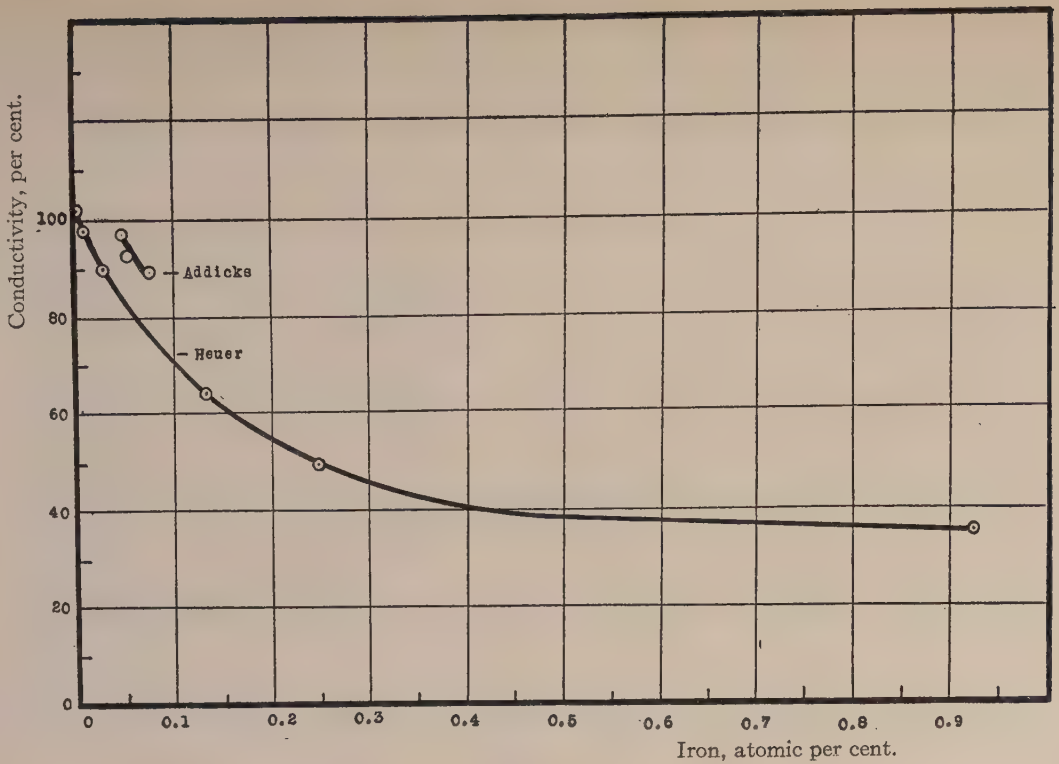

FIG. 4

Effect of Iron on Conductivity of Copper.

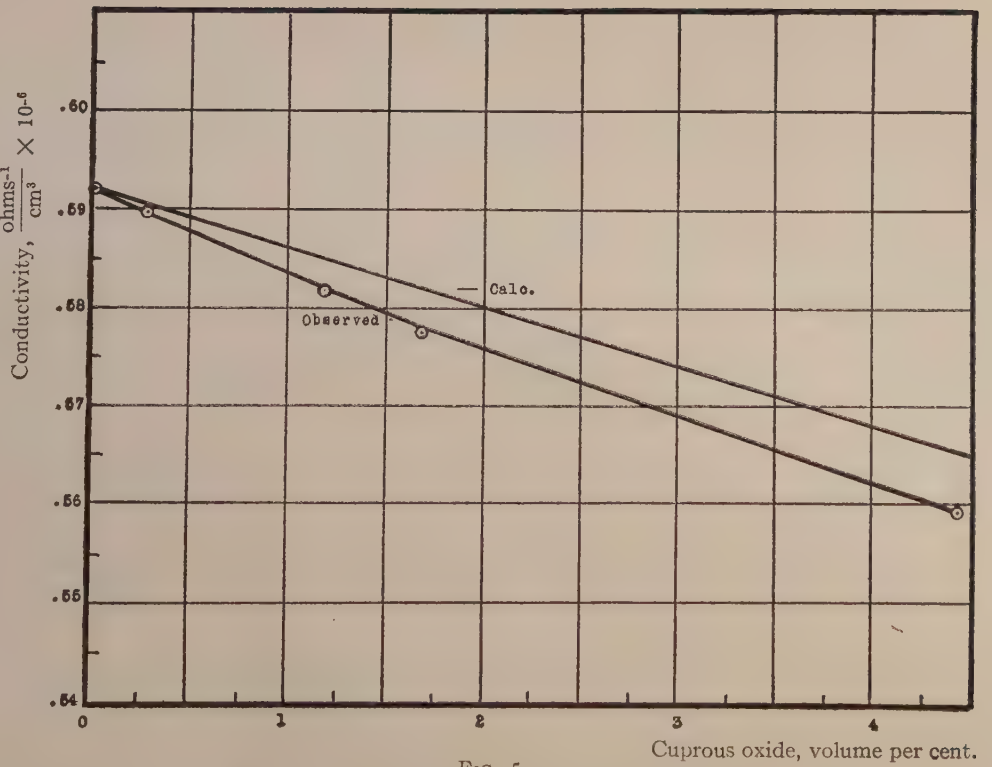

FIG. 5

Effect of Cuprous Oxide on Conductivity of Copper.

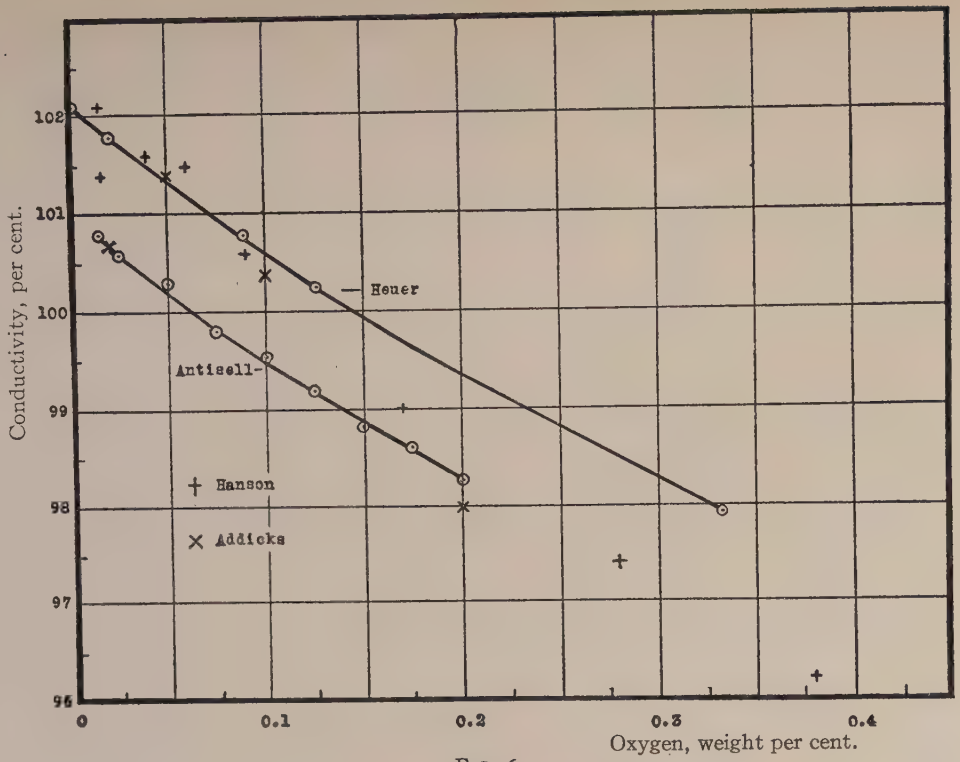

FIG. 6

Effect of Oxygen on Conductivity of Copper.

Sci. Paper 148, 1910) for several samples of "pure" copper. Their highest value is 101.88%, obtained for electrolytic copper, melted in vacuo in an Acheson Graphite crucible, drawn and tested as annealed wire. A piece of native Lake copper formed into wire without melting and tested in the annealed state yielded 101.87% conductivity. Their best value of several samples of electrolytic copper drawn to wire without melting and annealed is 101.60%. Meissner (*Ann. der Physik*, 47 (1915), 1001) observed 102.2% conductivity in a piece of electrolytically deposited wire which was carefully filed and ground to circular cross-section and tested without drawing or annealing. This sample, however, cannot be regarded as statistically equivalent to the polycrystalline aggregate obtained in wires which have been drawn and annealed. The electrolytic crystals may exhibit some preferred orientation and tend thereby to increase the conductivity toward the higher value of the copper single crystal.

The data for the binary system copper-cuprous oxide are assembled in Table 2. The curve in Fig. 5 represents the relation of conductivity to volume per cent of cuprous oxide, calculated for a density of the oxide 6.0. Comparison is made to conductivity values calculated from the law of Le Chatelier which requires that in systems whose components are insoluble in each other, the conductivity should be a linear function of the volume relationship. The observed conductivity is slightly lower than the calculated value due to the occurrence of the cuprous oxide in the test wires as elongated spherical globules. If the oxide were present as cylinders, extending in uniform cross-section throughout the length of the wire sample, the calculated and observed values should coincide.

In Fig. 6 the conductivity is plotted against weight per cent of oxygen. Data of Hanson (*Jl. Inst. Metals*, 30, (1923), 197); Antisell (*Tr. A. I. M. E.*, 64 (1921), 432) and Addicks (*op. cit.*) are plotted for comparison. Antisell's figures seem to be the only ones capable of being reduced to a smooth curve. The curve indicated parallels closely the curve presented here, averaging perhaps 1.1% lower in conductivity. The lower conductivity is probably due to impurities other than oxygen in Antisell's metal.

The data for the ternary melts are presented in Table 3. The pronounced effect of oxygen is at once apparent. Ostensibly the initial charges contained iron and oxygen sufficient to exceed the activity product of Equation (13). Considerable ferrous oxide was, therefore, eliminated from the liquid alloys. For the residual iron and oxygen content, the product—Mol Fraction Iron × Mol Fraction Cuprous Oxide—has been computed. There is shown considerable constancy in these values, supporting

TABLE 3

Melt No.	Iron charged, per cent	Oxygen charged, per cent	Iron found, per cent	Oxygen found, per cent	Sulphur, per cent	Copper, per cent
14	0.13	0.02	0.0133	0.0035	0.0003	99.982
16	0.11	0.02	0.0115	0.0040	0.0002	99.984
17	0.05	0.02	0.0061	0.0083	0.0003	99.989
13	0.10	0.04	0.0058	0.0273	0.0003	99.966

Melt No.	Mol Fraction Fe × Mol Fraction Cu_2O	Conductivity (observed), per cent	Conductivity calculated from Oxygen Content (neglecting Fe), per cent	Conductivity Lowering due to Iron, per cent	Equivalent Iron in Solid Solution, per cent	Microstructure as cast
14	2.10×10^{-6}	101.80	102.05	0.25	0.0004	No eutectic
16	2.08×10^{-6}	101.85	102.05	0.20	0.0003	No eutectic
17	2.29×10^{-6}	102.0	102.0	0.0	None	Copper plus eutectic
13	7.16×10^{-6}	101.85	101.7	−0.15	None	Copper plus eutectic

the tenets of Equation (13). Deviation is evident at higher oxygen values. The iron does not seem to be sufficiently eliminated. Perhaps ferrous oxide remains in the liquid melt, either as a true solution or in colloidal dispersion.

The iron which survives the attack of the cuprous oxide in dilute solution at 1125° C. is subjected to stronger oxidizing action during freezing of the melt. The cuprous oxide content of the liquid rises and reaches 3.45% at the eutectic composition. More ferrous oxide forms but in this reaction probably remains in the alloy as non-metallic inclusion. The unoxidized iron enters into solid solution with the copper.

Melts 14 and 16 show no cuprous oxide eutectic. The reaction has proceeded to the extinction of the cuprous oxide phase, the iron remaining above its equilibrium value. The electrical conductivity of the alloys indicates perhaps 0.0005% iron in solid solution. Melts 13 and 17 show the presence of oxide eutectic. The reaction has approached closer to the iron equilibrium. The electrical conductivity shows no lowering which may be ascribed to iron. There is certainly less than 0.0001% iron in the solid solution.

Summary

(1) Thermodynamic calculations are presented in this paper which question the validity of the existing measurements of the electrical conductivity of dilute metallic solid solutions in copper.

(2) A revision for the dilute solid solutions of iron in copper is made, basing the measurements upon the ternary system copper-iron-oxygen.

(3) The conductivity of copper-rich alloys in the binary system copper-iron is determined in the absence of oxygen and other elements.

(4) The conductivity of copper-rich alloys in the binary system copper-cuprous oxide is determined in the absence of iron and other elements.

(5) The conductivity of copper-rich alloys in the ternary system copper-iron-oxygen is determined.

(6) The conductivity of a very pure sample of copper is found to be 102.1 per cent.